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Oxidation Behavior of NiAl-TiB_2 Coatings Prepared by Electro-thermal Explosion Ultrahigh Speed Spraying

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Abstract

The electro-thermal explosion ultrahigh speed spraying technology was employed to prepare the NiAl coatings with 0, 10, and 20 wt.% TiB_2 on the Ni-based super-alloy substrate. The Microstructure, phase structure, and hardness of coatings were analyzed by scanning electron microscopy with energy dispersive X-ray spectrometry, X-ray diffraction, and Vickers micro-hardness tester, respectively. The results showed that the coatings had dense microstructure with submicron grains. The addition of TiB_2 as a particulate reinforcement increased the hardness of NiAl. The isothermal oxidation test of coatings at 1000 °C for 140 h in air was investigated. The results showed that the oxidation resistance of NiAl coatings was higher than that of NiAl-TiB_2 coatings at high temperature. The oxides and morphologies of the above coatings were investigated. The Al_2O_3 was formed on NiAl coating surface, while Al_2O_3 and TiO_2 were formed on NiAl-TiB_2 coating surface after oxidation.

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Keyword: Electro-thermal explosion ultrahigh speed spraying; NiAl-TiB_2 coatings; Oxidation behavior

1. Introduction

The inter-metallic compound NiAl possesses many attractive properties such as low density (5.9 mg/cm^3), high melting point (1640 °C), high modulus of elasticity (193 GPa), and good thermal conductivity [1]. In addition, the NiAl has excellent oxidation resistance at very high temperature (~1000 °C). The oxidation of NiAl is characterized by the formation of an adherent and protective α-Al_2O_3 scale, whose growth is controlled by relatively slow diffusion of oxygen grain boundary. However, the NiAl has poor fracture toughness at room temperature and inadequate high temperature strength, which makes it unsuitable for high temperature structural application. The NiAl can be used as high temperature protective coatings.

The methods for improving the mechanical properties of inter-metallic compounds include their alloying with other elements and reinforcing with particles of carbides, oxides, and borides. The mechanical properties and high-

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temperature strength of NiAl can be improved by the addition of dispersed particulates of relatively harder compounds, such as TiB_2, ZrB_2, CeO_2, or ZrO_2 [2]. TiB_2 possesses high melting point (2900 °C), high hardness, high elastic modulus (370 GPa), high electrical conductivity, and relatively low coefficient of thermal expansion [3]. The hardnesses of NiAl and TiB_2 are about 3 and 27 GPa, respectively. The addition of TiB_2 as a particulate reinforcement to NiAl can increase the hardness. However, the rate of oxidation of NiAl at high temperature increases with TiB_2 content [4].

The NiAl coatings have been used in a wide variety of engineering applications such as high temperature protective coatings, where the base material provides the necessary mechanical strength and the coatings provide the protection against both wear and oxidation. The NiAl is the basis of a family of oxidation and corrosion-resistant coatings that have been used on Ni-based and Co-based super-alloys [5].

The NiAl coatings can be prepared by aluminizing procedure, plasma spraying, electromagnetic guns, electron beam physical vapour deposition, and plasma-detonation technologies [2,6,7]. The plasma detonation devices are used for coating deposition, in which plasma jet rate reached 8000 km/s, energy density amounts 5×10^6 W/cm^2. These technologies have been successfully applied for fabrication of metallic Ni-Cr, Co-Cr, Ni-Al, Al-Co, metal-ceramic Cr_3C_2-Ni, WC-Co, and ceramic Al_2O_3 coatings [7].

The electro-thermal explosion ultrahigh speed spraying (EEUSS) can prepare coatings with dense microstructure, high hardness, low porosity, and good bonding with substrate. The EEUSS process is characterized by the duration of 10 ms, the highest pressure at the centre of exploding gas up to 7-10 GPa, a plasma temperature about 10^4 K, the speed of spraying droplets up to 3000-4500 m/s, an average cooling rate of droplets up to 10^7-10^9 K/s and a specific energy of more than 1 MJ/kg [8,9]. The surface of the substrate can be rapidly melted by the EEUSS particles with a temperature range of 3000-4000 °C. The bonding of coating-substrate is metallurgical.

In this investigation, the EEUSS technology was employed to prepare the NiAl coatings with 0, 10, and 20 wt.% TiB_2 on the Ni-based superalloy substrate. The microstructure and isothermal oxidation behavior of NiAl-TiB_2 coatings at 1000°C in air were investigated.

2. Experimental Procedure

The EEUSS technique and its equivalent circuit are described in detail before [10,11]. The substrate material is the Ni-based super-alloy with the nominal composition varied within the following ranges: (wt.%) 19.0-22.0Cr, 0.35-0.75Al, 0.35-0.75Ti, 1.80-2.30Mo, 0.90-1.30Nb, ≤0.012S, ≤0.08C, ≤3.0Fe, ≤0.40Mn, ≤0.80Si, ≤0.02P, while Ni being the balance. The surfaces of substrates are cleaned and degreased.

The sprayed materials are B powder, Ni, Al, or Ti foil with a thickness of 20 μm. The sizes of B particles are 48-75 μm. The purity of elements is all about 99.9 wt.%. The Ti-Ni-Al composite tube with the boron powders is pressed to form a cored foil. The spraying parameters are the same as those in reference 11. This way, the NiAl (it is in-situ formed by Ni and Al foil) coatings with 0, 10, and 20 wt.% TiB_2 (also in-situ formed by Ti and B) are prepared on the Ni-based super-alloy substrates, respectively. The thickness of coatings is in the range of 30-70 μm. During spraying, the B powder, Ti, Ni, and Al foils are heated rapidly to the temperatures above their melting points. The melted droplets are sprayed to the surface of the substrate and rapidly solidified.

Scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) are used to identify the microstructure and morphology of coatings before and after oxidation. The microhardness of the polished cross-section of the coatings is measured using a FM-300 Vickers' hardness tester. The load of 200 g and holding time of 15 s are applied. The experimental data are collected from the average of three measured data at each point with an error of ±5 %.

In order to investigate the oxidation behavior of coatings prepared using EEUSS technology, cyclic oxidation test is performed in a muffle furnace. All specimens are weighed (±0.0001g) and measured (±0.005mm) before oxidation test. The samples in circular Al_2O_3 crucible are put into muffle furnace at 1000 °C. During the test, specimens are intermittently taken out from the furnace, air-cooled, cleaned and followed by weighing. The temperature is held constantly at 1000°C throughout the test. The oxidation kinetics is determined at 1000 °C for 140 hrs in air.

3. Results and discussions

3.1. Microstructure and microhardness of the coatings

According to the XRD analysis of EEUSS coating surface as shown in Fig.1(a), three phases are detected in pure NiAl coating, which are the main phase NiAl, a small amount of Ni_3Al and Al, respectively. In NiAl-10%TiB_2 coating, the main phase NiAl is synthesized, a small amount of TiB_2 and Al are also found. In NiAl-20%TiB_2 coating, the NiAl and TiB_2 main phases are synthesized, and a small amount of Al and Ni_3Al are also found. In terms of thermo-physical properties, the NiAl is more suitable for the high temperature applications than Ni_3Al. The oxides of Ni, Al, or Ti are not detected in coatings, because during the electric explosion, the mixture consists of high-pressure air and molten particles, which are ejected from the bottom of the exploding chamber to the substrate within 50 μs. The flight time of the particles is short and the sprayed particles are protected by its self-explosion gas.

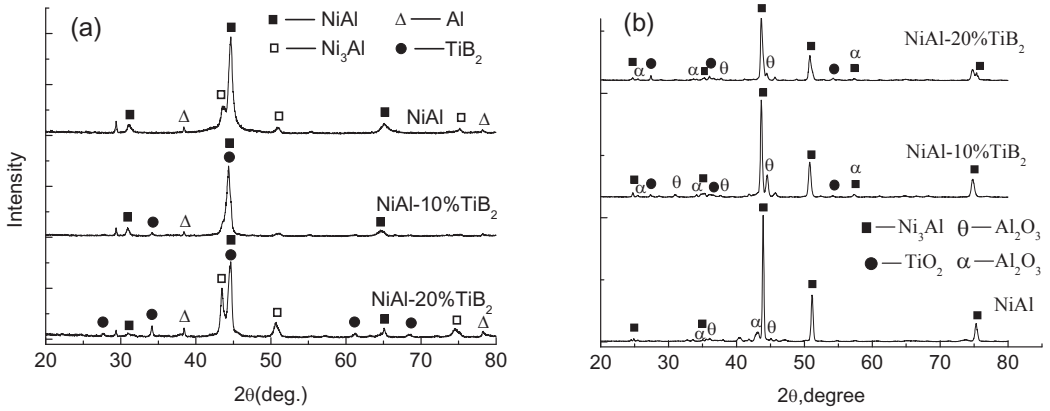

Fig.1 XRD patterns of the NiAl-TiB_2 coating surface: (a) before oxidation; (b) after oxidation

The coatings have dense microstructure with submicron grains. The reason is that the molten EEUSS particles resulting from high pressure, high temperature, and high speed impact on the surface of substrate then solidify quickly. The EEUSS technique plays a dominant role in improving the mechanical properties by controlling grains' sizes.

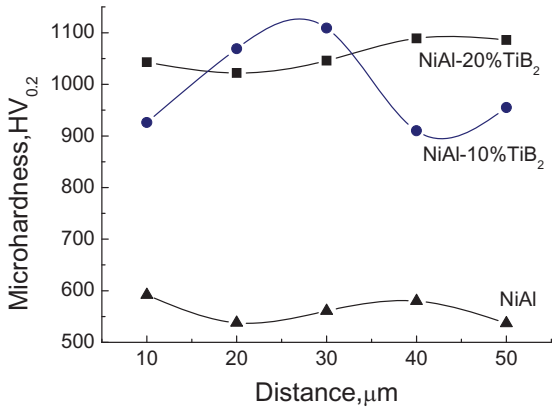

Fig.2 The microhardness of the NiAl-TiB_2 coatings

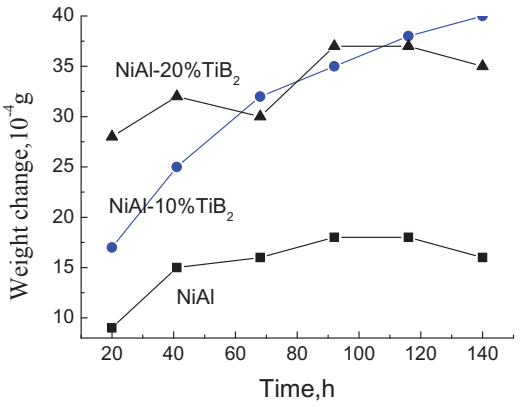

Fig.3 Oxidation dynamics curve of coatings

Fig.2 shows that the microhardness of the NiAl-TiB_2 composite coatings increases relative to NiAl coating, and hardness of NiAl increases significantly after addition small amount of TiB_2. The average micro-hardness of NiAl, NiAl-10%TiB_2, and NiAl-20%TiB_2 coatings are found to be about 562, 994, and 1057 $HV_{0.2}$, respectively. Because

hardness of NiAl is about 300 HV, while that of TiB_2 is about 2700 HV, high hardness and dispersed phase hardening of TiB_2 play an important role in improving hardness. The distance of abscissa in Fig.2 is between measured points in coatings. The fluctuant hardness in coatings is usually caused by distribution of phases, thickness of coatings, microcracks, and measurements error. The microhardness of the bonding zone of coatings-substrate is about 350 HV, which is lower than that of the coatings, but higher than that of the substrate (about 250 HV). The hardness for NiAl, NiAl-10%TiB_2, and NiAl-20%TiB_2 composites produced by reactive powder processing is found to be about 300, 340, and 450 HV, respectively [1]. The micro-hardness of NiAl and NiAl-40wt.%TiB_2 compounds by self-propagating high-temperature synthesis is found to be 394±37 $HV_{0.2}$ and 967±104 $HV_{0.2}$, respectively [2]. Thus, the microhardness of coatings is also related to the preparing technology. Compared with other methods, the EEUSS has many unique advantages.

3.2. The oxidation of the coatings

3.2.1. Oxidation kinetics

Fig.3 shows the kinetics curve of cyclic oxidation of the coatings exposed in air at 1000°C for 140 hrs. The weight gain *vs*. time plots show that the NiAl and NiAl-TiB_2 coatings display close to parabolic behavior. For NiAl-TiB_2 coatings parabolic behavior follows an initial period of higher-order behavior. The weight gain of NiAl coatings with 0, 10, and 20 wt.% TiB_2 is found to be 1.6, 4, and 3.5 mg/cm^2, respectively. It is obvious that the addition of TiB_2 accelerates the oxidation of NiAl coating at high temperature. For the NiAl-20%TiB_2 coating, at about 60 hrs, mass loss is observed due to evidence of serious oxides scale spallation. The high weight change of the NiAl-TiB_2 coatings shows that the oxidation aided by spallation would be more severe during cyclic oxidation. However, no obvious spallation could be observed for the NiAl coating during the whole test period. Hence, the oxidation resistance of NiAl coating is higher than that of NiAl-TiB_2 coatings at 1000°C. It shows that the addition of TiB_2 as a powerful reinforcement increases the hardness, but decreases oxidation resistance of NiAl coating. These results correspond with those reported in the literature 4.

3.2.2. Oxidation products of coatings surface

Fig.4 shows the surface morphology of the coatings after cycle oxidation at 1000°C for 140 hrs. It can be seen that the whisker-like meta-stable θ-Al_2O_3 appears on surface of coatings. Based on the high aluminium activity, NiAl forms only α-Al_2O_3 at 800 °C. In fact, the primal oxide of Al is θ-Al_2O_3. The study indicated that the most of θ-Al_2O_3 grains transformed into α-Al_2O_3 after 3 hrs oxidation at 950 °C [12]. The transformation from θ-Al_2O_3 to α-Al_2O_3 is generally observed to begin at the coating-oxide interface. Therefore, the oxide film may have θ-Al_2O_3 whiskers at the film-gas interface, but still consists almost entirely of α-Al_2O_3 beneath this outer layer [13]. The oxidation kinetics is controlled by ionic diffusion through the α-Al_2O_3, leading to a low oxidation rate. The Al_2O_3 formed at coating surface indicates that the oxygen diffuses more slowly than aluminum, so it is assumed that the principal route of oxygen diffusion is along grain boundaries, while that of Al diffusion is along grain boundaries and bulk.

The EEUSS technology can prepare coatings with the sub-micrometer size grains, the micro-crystallization accelerate the phase transformation from the meta-stable θ-Al_2O_3 with a high growth rate to the stable α-Al_2O_3 with a low growth rate in the formed film [13], which may be due to increased number of nucleation rate because of the great number of grain boundaries. The small amount of Cr diffuses from substrate to the coatings during high temperature oxidation, which accelerates the transformation of θ-Al_2O_3 to α-Al_2O_3 by increasing the nuclei of α-Al_2O_3. The experiment proves that even at the initial oxidation stage Cr plays an important effect on accelerating alumina transformation [12]. At very early oxidation stage, the content of Cr diffused from substrate to coatings is less, the effect of Cr for the transformation of θ-Al_2O_3 to α-Al_2O_3 is inconspicuous. With oxidation time increasing, the amount of Cr in coatings increases, which will accelerate the transformation of θ-Al_2O_3 to α-Al_2O_3.

Oxides of the coating surface have been confirmed by XRD, as shown in Fig.1(b), it revealed that the dominating oxides of Al are α-Al_2O_3 and θ-Al_2O_3. Fig.4(a) also shows that the principal oxides of NiAl coating surface are whiskers θ-Al_2O_3 scale, which are the same as those in reference 13. In addition, Cr and Ni atoms of the substrate are diffused to coatings during high temperature oxidation and oxidized. A small content of Cr_2O_3 and

NiO are also found on the surface of three kinds of coatings. Figs.4(b) shows that the morphologies of the coating surface after oxidation are various, which revealed different oxidation products, and distributing of oxides is inhomogeneous. The dominant phase in the coatings changes from β-NiAl phase to γ′-Ni_3Al phase after oxidation.

The addition TiB_2 to NiAl results in a more complex oxide film morphology. The most obvious change is the appearance of discrete TiO_2 crystallites. The Al_2O_3 and scattered crystallites of columnar TiO_2 are formed on NiAl-TiB_2 coating surface after oxidation at 1000°C. The crystallites of TiO_2 appear singly and in aggregates, as shown in Fig.4(b). The TiO_2 crystallites extend outward the film and are prone to spalling. Their appearance on the oxide surface is evidence of outward titanium diffusion within the coatings. The fraction of the surface covered by TiO_2 appears qualitatively to be a function of TiB_2 concentration in the coatings, not that of oxidation temperature. No TiO_2 crystallites are observed on the 20% TiB_2 at 1200°C scale surface [4].

The micro-cracks are usually caused by different coefficient of thermal expansion between substrate and coatings during spraying. When the initially formed θ-Al_2O_3 film transforms to α-Al_2O_3, the volume reduces, also leading to film cracking. Fig.4 shows that the micro-cracks in coatings have been cured after oxidation. Almost whole surface of the samples is covered by oxides. The oxide film is beneficial for improving the oxidation resistance of coatings.

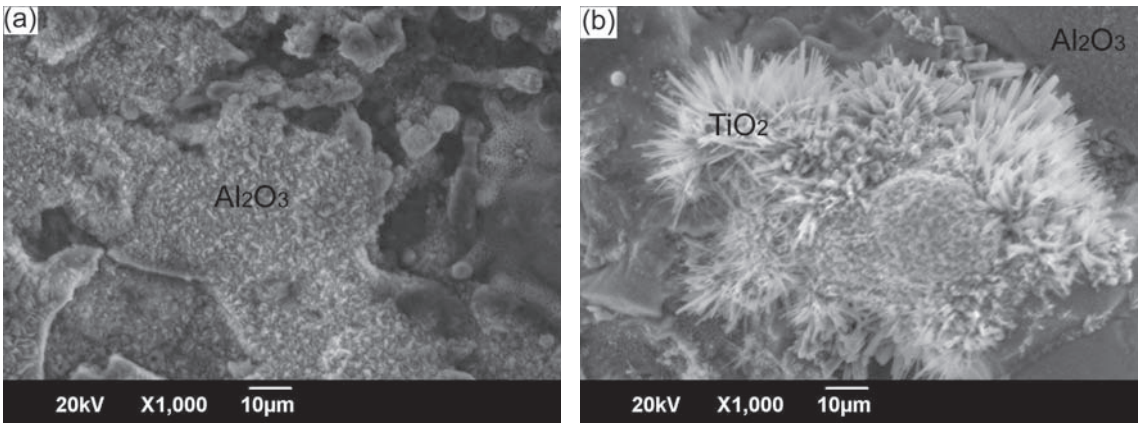

Fig.4 Surface micrographs of coatings after oxidation at 1000°C for 140 h: (a) NiAl coating; (b) NiAl-10%TiB_2 coating

3.2.3. Oxidation of the cross-section of the coatings

Fig.5 shows the EDS mappings of O, Al, and Cr of the cross-section of NiAl-10%TiB_2 coating oxidized at 1000°C for 140 hrs. The Al atoms diffuse to surface, pores, cracks, and interface, are oxidized and form Al_2O_3. The Cr atoms diffuse from the substrate to surface and interface of coatings during high temperature oxidation, while the diffusing content is small in the course of spraying. The films grown on coatings are continuous and also appear in good contact with their substrates. The submicron coatings favor a faster outward diffusion of Al along high-diffusivity paths (a great number of grain boundaries), so an alumina film of compact may quickly form.

Based on the analyses of thermodynamic data, the free energy of formation of Al_2O_3 is the lowest, followed by those of Cr_2O_3 and TiO_2 at all temperatures of interest. The protection of Cr_2O_3 film was not as good as that of Al_2O_3 at 1000 °C. The titanium diffuses outward the coatings through the oxide film and form TiO_2 at the outer surface, so the rate of oxidation increases with TiB_2 content.

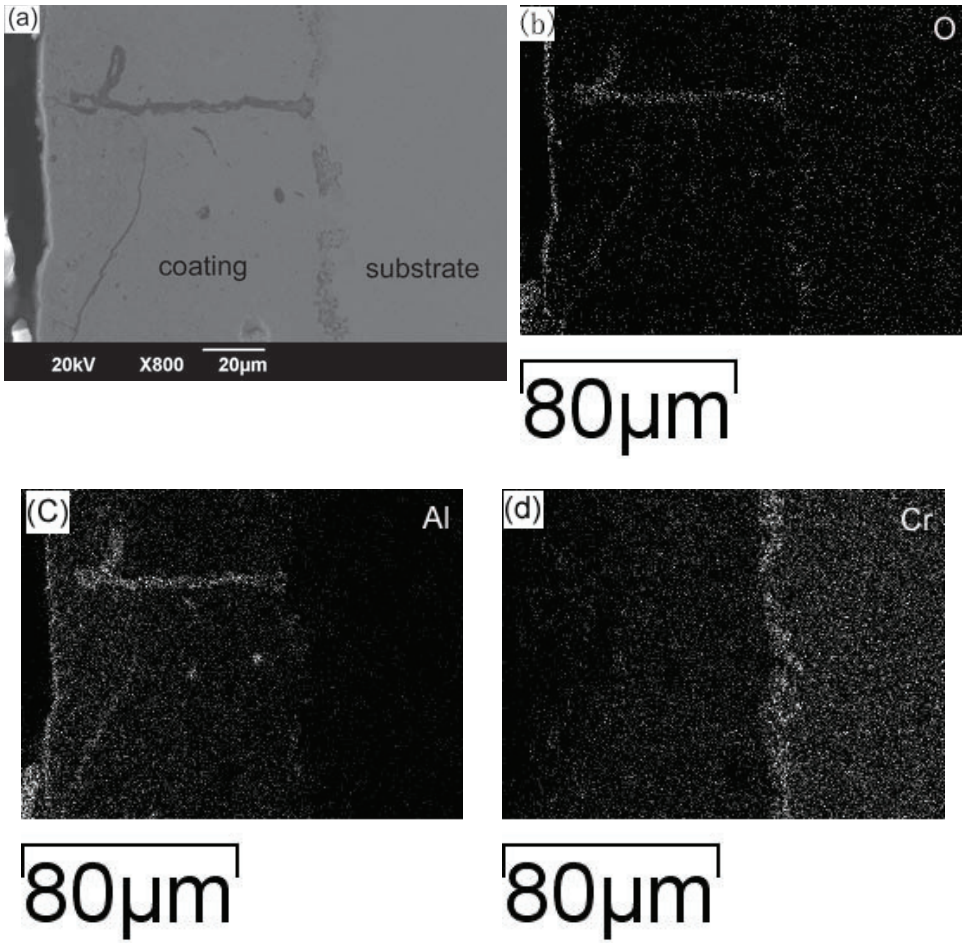

Fig.5 Photomicrographs and EDS pattern of cross-section of NiAl-10%TiB_2 coatings

4. Conclusions

NiAl-TiB_2 composite coatings were synthesized on Ni-based super-alloy substrate by EEUSS technology. The coatings had dense microstructure with submicron grains. The addition of TiB_2 as a particulate reinforcement increased the hardness of NiAl coating. The average micro-hardness of NiAl coatings with 0, 10, and 20 wt.% TiB_2 were found to be about 562, 994, and 1057 $HV_{0.2}$, respectively.

The oxidation kinetics showed that the NiAl-TiB_2 composite coatings were inferior to NiAl ones at high temperature oxidation. Thus, TiB_2 particles increased the oxidation rate of NiAl. The principal oxides of NiAl coating surface were whiskers θ-Al_2O_3 film. NiAl-TiB_2 coating surface was an alumina-titania oxide film, and the film was not entirely protective.

5. Acknowledgements

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